



Sulfur dioxide inhibits calcium carbonate precipitation: Implications for early Mars and Earth

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[1] Recent studies have suggested a role for sulfur dioxide (SO₂) in maintaining relatively warm surface temperatures on early Mars. Here we show experimentally, that SO₂ concentrations orders of magnitude lower than those required for it to have been of climatic importance strongly affect the aqueous chemistry and the precipitated mineral assemblage. At near-neutral pH, part-per-billion concentrations of SO₂ prevent the formation of calcium carbonate in favor of hannebachite, a hydrated calcium sulfite. In the presence of iron, possible precursors to phyllosilicate minerals and iron carbonate co-precipitate with hannebachite. This provides an explanation for the existence of early Noachian phyllosilicates in the apparent dearth of outcrop-scale calcium carbonates. Oxidation of this precipitated assemblage produces sulfates, iron oxides and acidity, consistent with evidence for late Noachian–early Hesperian acid-sulfate dominated environments. For early Earth, the results allow placing an upper limit on atmospheric SO₂ concentrations for any period in which carbonates exist in the geologic record.

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1. Introduction

[2] SO₂ is abundant in terrestrial volcanic emissions and was likely at least as abundant in early Martian emissions [Gaillard and Scaillet, 2009; Johnson et al., 2008]. Recent photochemical studies indicate that during episodes of vigorous volcanic activity, the atmospheric lifetime of SO₂ may have been sufficiently long for it to have helped maintain liquid water on the surface of Mars [Johnson et al., 2008; Halevy et al., 2007; S. S. Johnson et al., The fate of SO₂ in the ancient Martian atmosphere: Implications for transient greenhouse warming, submitted to *Journal of Geophysical Research*, 2009] and perhaps to have regulated the climate through a negative feedback between the atmospheric abundance of SO₂ and the rate of chemical weathering of silicate minerals [Halevy et al., 2007]. Like CO₂, SO₂ is a weak diprotic acid (sulfurous acid or H₂SO₃) whose conjugate base, sulfite (SO₃²⁻), can form a mineral with calcium. This mineral, hannebachite (CaSO₃ × ½H₂O), is ~90 times more soluble than the least soluble calcium carbonate (calcite), but SO₂ is much more soluble than CO₂ and a much stronger acid (Table 1). Accounting for this,

thermodynamics predict that at ratios of the partial pressure of SO₂ to CO₂ (*p*SO₂:*p*CO₂) as low as 5.3 × 10⁻⁸ hannebachite saturates at Ca²⁺ concentrations lower than those required for calcite saturation [Halevy et al., 2007]. This means that ~50 parts-per-billion (ppb) SO₂ in 1 bar of CO₂, for example, are enough to prevent calcite from precipitating, not due to acidification of the water, but because hannebachite precipitation buffers the Ca²⁺ concentration at values too low for saturation and precipitation of calcite.

[3] Kinetic factors, which commonly influence the precipitated mineral assemblage, have never been investigated for a mixed sulfite-carbonate system. It is therefore difficult to assess the relevance of the above thermodynamic prediction to early Mars. To address this we conducted a series of mineral precipitation experiments from O₂-poor solutions saturated with both calcite and hannebachite and found that inhibition of carbonate precipitation occurs at even lower values of *p*SO₂:*p*CO₂ than predicted. This implies that even if SO₂ were not abundant enough to influence Noachian climate, it may provide an explanation for the scarcity of carbonate minerals at outcrop abundance [Christensen et al., 2001], other than in laterally restricted environments that may not represent prevailing early Martian surface conditions [Ehlmann et al., 2008]. Because this explanation for the scarcity of carbonates does not require acidic conditions, it may also account for the occurrence of early phyllosilicates [Poulet et al., 2005], which require near-neutral pH to form [Velde, 1995].

2. Methods

[4] The experiments were conducted in sealed borosilicate glass bottles. Oxygen was removed by bubbling purified N₂ through the water for ~60 minutes before sealing. The desired experimental conditions (aqueous concentrations, *p*SO₂:*p*CO₂, ionic strength, etc.) were achieved by adding precalculated amounts of reagent-grade salts. Also controlled by the amount of reagents added was the degree of saturation of the different minerals ($\Omega_{C_c A_a} \equiv [C]^c [A]^a / K_{sp}$, where [C] is the aqueous concentration of the cation C, [A] is the concentration of the anion A, c and a are their respective stoichiometric amounts in the mineral C_cA_a and K_{sp} is that mineral's equilibrium solubility product constant). Sealed solutions were stirred in a temperature-controlled environment until precipitates formed or until termination at 10–20 days. Precipitates were freeze-dried, imaged by scanning electron microscope (SEM) and their mineralogy determined by X-ray diffraction. A detailed description of the experimental and analytical methods, the materials used and the experimen-

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Table 1. Equilibrium Constants at 25°C for the Carbonate and Sulfite Systems^a

Equilibrium Constant (25°C)	SO ₂	CO ₂
log(K _H)	+0.17	-1.47
log(K _{a1})	-1.86	-6.34
log(K _{a2})	-7.21	-10.33
log(K _{sp})	-6.51	-8.48

^aK_H is Henry's law constant (mole l⁻¹ atm⁻¹), describing the solubility of gas in water. K_{a1} and K_{a2} are the first and second acid dissociation constants, respectively. K_{sp} is the solubility product constant of hannebachite (CaSO₃ × ½H₂O) and calcite (CaCO₃).

tal conditions, as well as sample X-ray diffractograms and SEM images are in the auxiliary material (AM).¹

3. Results

3.1. Ca–Na–Cl–CO₂–SO₂ Solutions

[5] In a Ca–Na–Cl–CO₂–SO₂ system with an ionic strength of 0.2 and at 25 ± 1°C, we varied $p\text{SO}_2:p\text{CO}_2$ between 1×10^{-8} and 1×10^{-7} , corresponding to a ratio of the degrees of saturation of calcite and hannebachite ($\Omega_{\text{cal}}:\Omega_{\text{han}}$) between ~0.7 and ~5.1 (Figure 1a). Hannebachite precipitated down to $p\text{SO}_2:p\text{CO}_2$ of $\sim 1.3 \times 10^{-8}$, about a factor of 4 lower than the thermodynamic prediction, and despite values of Ω_{cal} as high as ~14 (Ω_{han} required for precipitation was ~3). At $p\text{SO}_2:p\text{CO}_2$ of $\sim 1.3 \times 10^{-8}$ the solution precipitated both hannebachite and vaterite, the most soluble CaCO₃ polymorph, followed by vaterite only at lower $p\text{SO}_2:p\text{CO}_2$. This transition occurs very close to the thermodynamic equilibrium phase boundary between hannebachite and vaterite (calculated at $p\text{SO}_2:p\text{CO}_2$ of $\sim 1.4 \times 10^{-8}$). Although experimental studies report quantitative transformation of vaterite to the more stable polymorphs of CaCO₃ (aragonite or calcite) within ~70 hours [Nissenbaum *et al.*, 2008], sealed solutions left to stir for 120 hours after precipitates formed still yielded only vaterite. This, in combination with the fact that CaCO₃ formed only at or below the thermodynamic boundary between hannebachite and vaterite (i.e. where $\Omega_{\text{vat}}:\Omega_{\text{han}} \geq 1$), may indicate that sulfite, bisulfite or their aqueous complexes destabilize aragonite and calcite relative to vaterite, like certain polyelectrolytes are known to do [Xu *et al.*, 2008].

[6] Repeated experiments with the addition of basaltic dust revealed that contact with pre-existing rock fragments does not lower kinetic barriers to CaCO₃ nucleation enough to affect the chemical composition of the precipitates; CaCO₃ still formed only where $\Omega_{\text{vat}}:\Omega_{\text{han}} \geq 1$. However, the basaltic dust destabilized vaterite in the CaCO₃-yielding experiments and resulted in mixtures of aragonite and calcite. In addition, the degree of saturation required for precipitation in some of the experiments was lower, consistent with experimental evidence that pre-existing mineral grains assist nucleation [Kralj and Vdovic, 2000].

3.2. “Martian” Solutions

[7] To simulate solutions that evolved at or near Mars' surface as water interacted with basalt, we conducted experiments with SO₄²⁻, Fe²⁺ and Mg²⁺ in addition to the aforementioned components, at 25 ± 1°C. The ratio

Fe:Mg:Ca was initially 2:1:1, representative of Martian basalts [McSween *et al.*, 2009], but neglecting the variability expected during chemical weathering of a planetary surface, which depends on the water-to-rock ratio, the composition, mineralogy and crystallinity of the weathered rocks [Tosca *et al.*, 2004], among other factors. The ratio S:Cl resulting from the salts used in the preparation of the solutions was ~2:1, somewhat lower than the average value from the MER landing sites of ~5:1 [Yen *et al.*, 2005]. These solutions precipitated mixtures of siderite (FeCO₃) and Fe-oxides/hydroxides, either directly at pH ≤ ~7.1 or via a carbonate green rust precursor ($[(\text{Fe}^{2+}, \text{Mg}^{2+})_{(1-x)}\text{Fe}_x^{3+}(\text{OH})_2]^{x+} \times [\frac{2}{3}\text{CO}_3^{2-} - y\text{H}_2\text{O}]^{x-}$ with $\frac{1}{4} \leq x \leq \frac{1}{3}$ according to Genin and Ruby [2004]) at higher pH. The precipitation of the Fe-bearing phases removed alkalinity from the solutions and lowered the pH by a few tenths of a pH unit, enough to depress Ω_{cal} and Ω_{han} to values too low for precipitation of a Ca-bearing phase. At decreased Fe²⁺ concentrations (Fe:Mg:Ca of 1:1:1 and 1:2:2), appropriate to surface solutions that had already lost some iron, hannebachite precipitation accompanied the Fe-bearing phases at all values of $p\text{SO}_2:p\text{CO}_2$ examined (Figure 1b). The absence of a CaCO₃ phase even at very low $p\text{SO}_2:p\text{CO}_2$ is due to the buffering of the CO₃²⁻ concentration by siderite saturation. No magnesian

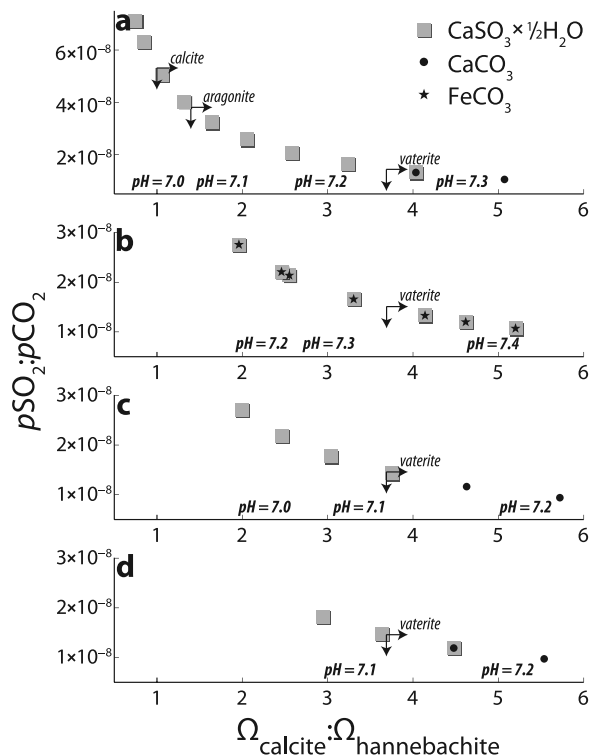


Figure 1. (a) Minerals precipitated from (a) Ca–Na–Cl–CO₂–SO₂ system with an ionic strength of 0.2, (b) water representing weathering of Martian basalt, and artificial seawater with (c) 28 mM SO₄²⁻ and (d) 1 mM SO₄²⁻. Squares, circles, and stars indicate CaSO₃ × ½H₂O (hannebachite), CaCO₃ (vaterite, aragonite, or calcite), and FeCO₃ (siderite), respectively. The values of $\Omega_{\text{cal}}:\Omega_{\text{han}}$ above which (and $p\text{SO}_2:p\text{CO}_2$ below which) thermodynamics predict vaterite, aragonite, and calcite are marked with arrows. The initial pH of the solutions is shown at the bottom of each graph.

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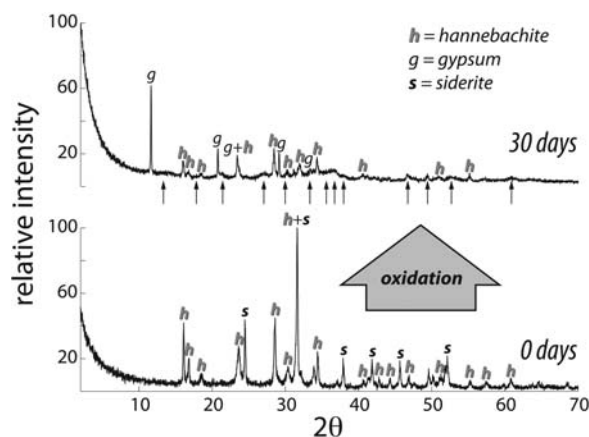


Figure 2. Oxidation of a mixture of hannebachite and siderite to gypsum and Fe-oxides/oxyhydroxides. The diffractograms were obtained (bottom) immediately and (top) 30 days after filtering. The arrows mark features associated with the diffraction peaks of several Fe-oxides/oxyhydroxides, including goethite, lepidocrocite, hematite, and magnetite. These features are in most cases broad, indicating small or poorly crystalline material.

phase reaches saturation under the experimental conditions explored. Kieserite ($\text{MgSO}_4 \times \text{H}_2\text{O}$) was closest to being saturated, followed by trihydrated magnesium sulfite and finally the Mg-carbonate magnesite ($\Omega \sim 10^{-1}$, $\sim 10^{-4}$ and $\sim 10^{-5}$, respectively).

[8] Oxidation of moist mixtures of hannebachite and siderite yielded gypsum ($\text{CaSO}_4 \times 2\text{H}_2\text{O}$), and mixtures of several small-grained or poorly crystalline Fe-oxides/oxyhydroxides within less than 30 days (Figure 2). This is consistent with experimental oxidative weathering of Fe-bearing minerals [Chevrier *et al.*, 2006], as well as with orbital and ground-based detection of sulfate minerals in association with Fe-oxides [McLennan *et al.*, 2005; Clark *et al.*, 2005; Bibring *et al.*, 2007; Morris *et al.*, 2006].

3.3. Artificial Seawater

[9] Volcanic emission of SO_2 into an O_2 -poor, CO_2 -rich atmosphere occurred also on early Earth. To examine the mineral assemblage expected to precipitate out of an early ocean, we conducted experiments at $25 \pm 1^\circ\text{C}$ in artificial seawater with a sulfate concentration of 28 and 1 mM, appropriate for the present-day and for the Archean-Paleoproterozoic [Canfield, 1998], respectively. In both the SO_4^{2-} -rich and SO_4^{2-} -poor experiments CaCO_3 only precipitated at $p\text{SO}_2:p\text{CO}_2 \leq \sim 1.3 \times 10^{-8}$ (Figures 1c and 1d). As in the other experiments, CaCO_3 formed instead of hannebachite only in the thermodynamic stability field of vaterite. However, aragonite and not vaterite was the final polymorph of CaCO_3 in the seawater experiments, in agreement with experimental evidence that Mg^{2+} in concentrations comparable to modern seawater stabilizes aragonite, irrespective of substrate [Sabbides and Koutsoukos, 1993].

4. Discussion

[10] Our results show that for a wide range of solution compositions at 25°C , calcite precipitation is inhibited for

values of $p\text{SO}_2:p\text{CO}_2 \geq \sim 1.3 \times 10^{-8}$. This corresponds, for example, to SO_2 concentrations of ~ 13 ppb in a pure CO_2 early Martian atmosphere or to only ~ 3 ppb in a 1 bar early Earth atmosphere containing 20% CO_2 .

[11] At 0°C , as perhaps relevant even to the wetter episodes in Martian history [Shuster and Weiss, 2005], $\Omega_{\text{cal}}:\Omega_{\text{han}}$ calculated from thermodynamics equals unity at $p\text{SO}_2:p\text{CO}_2$ of $\sim 5.4 \times 10^{-9}$ (instead of $\sim 5.3 \times 10^{-8}$ at 25°C) and $\Omega_{\text{vat}}:\Omega_{\text{han}}$ equals unity at $p\text{SO}_2:p\text{CO}_2$ of $\sim 1.2 \times 10^{-9}$ (instead of $\sim 1.4 \times 10^{-8}$ at 25°C). Although some error in these calculations is expected due to the absence of reliable thermodynamic data for some of the sulfite/bisulfite-bearing complexes and minerals, the trend towards inhibition of carbonate precipitation at even lower values of $p\text{SO}_2:p\text{CO}_2$ than at 25°C is likely robust (see AM). This means that as little as ~ 1 ppb SO_2 in a nearly pure CO_2 atmosphere, for example, would have been enough to inhibit CaCO_3 precipitation on early Mars. Such atmospheric concentrations were likely reached during periods of even modest volcanic activity, given that a volcanic SO_2 outgassing rate of only $\sim 1.5 \times 10^7$ molecules $\text{cm}^{-2} \text{s}^{-1}$ (~ 100 times smaller than the present terrestrial rate) would have maintained ~ 10 ppb SO_2 on early Mars according to the SO_2 e -folding times in the study of Johnson *et al.* (submitted manuscript, 2009).

[12] The occurrence of phyllosilicates in parts of the oldest Noachian crust, laterally separated from sulfates in presumably younger terrains, has been argued to reflect an epochal change from near-neutral to acid-sulfate dominated surface conditions [Bibring *et al.*, 2006; Chevrier *et al.*, 2007]. However, an early period in which only phyllosilicates formed presents a significant mass imbalance because weathering of basalt produces large amounts of soluble cations such as Mg^{2+} and Ca^{2+} , which should have precipitated with anions such as CO_3^{2-} , SO_3^{2-} , SO_4^{2-} or Cl^- as water evaporated [Milliken *et al.*, 2009a]. The mineral assemblages precipitated in our “Martian” water experiments and their oxidation products provide insight into early weathering and aqueous alteration environments on Mars and may reconcile the spatio-temporal distribution of minerals with the requirement for mass balance.

[13] Surface environments with abundant Fe^{2+} and CO_3^{2-} , would precipitate siderite, which would later transform to Fe-oxides/oxyhydroxides as the Martian atmosphere became more oxidizing due to escape of hydrogen and carbon to space [Lammer *et al.*, 2003; Tian *et al.*, 2009]. The fate of iron was probably different in the subsurface. Carbonate green rust has a layered double-hydroxide structure, a high affinity for dissolved silica [Christiansen *et al.*, 2009] and a tendency to incorporate magnesium in substitution for iron [Genin and Ruby, 2004]. Similarly structured precipitates transform into phyllosilicates in the presence of dissolved silica [Harder, 1978], suggesting that in subsurface environments enriched in silica from basalt weathering and depleted in CO_3^{2-} due to limited contact with the atmosphere, green rust may have served as a template for Fe-Mg phyllosilicates [Tosca *et al.*, 2008a] instead of transforming into siderite.

[14] Finally, solutions in contact with the atmosphere and relatively enriched in Ca^{2+} and Mg^{2+} by precipitation of Fe-bearing phases (e.g. lakes or rising groundwater) would have precipitated hannebachite and no CaCO_3 if $p\text{SO}_2:p\text{CO}_2$ was even as low as $\sim 1 \times 10^{-9}$. Magnesium

sulfates are expected to have formed as well; even in an O₂-poor atmosphere some of the outgassed SO₂ is photo-oxidized to H₂SO₄, which would accumulate in Mg²⁺-rich surface water, leading to evaporative precipitation of Mg-sulfates. Mg-carbonates are highly undersaturated in our experiments ($\Omega \sim 10^{-5}$), but would likely form in special environments [Ehlmann et al., 2008]. More sulfates would form later in Mars' history as older sulfites were exposed to the oxidizing atmosphere. Aqueous oxidation of sulfites to sulfates [Halevy et al., 2007] and ferrous to ferric iron [Chevrier et al., 2006; Tosca et al., 2008b] where siderite co-precipitated with sulfites, whether in situ as the water table fluctuated [McLennan et al., 2005; Grotzinger et al., 2005] or during aqueous transport by oxidizing solutions, would have released acidity, caused dissolution or leaching of coexisting phyllosilicates and left deposits of sulfates, Fe-oxides and hydrated silica. The most soluble cations would perhaps form chloride minerals. This is consistent with the mineral assemblages observed in several locations and with evidence for acid-sulfate dominated environments on late Noachian–early Hesperian surfaces [McLennan et al., 2005; Clark et al., 2005; Grotzinger et al., 2005; Squyres and Knoll, 2005; Morris et al., 2006; Bibring et al., 2007; Hurowitz and McLennan, 2007; Milliken et al., 2008; Squyres et al., 2008; Osterloo et al., 2008].

[15] The apparent temporal separation of phyllosilicates from sulfates may be an artifact of incomplete sampling. Interbedded sulfates and phyllosilicates have been detected recently [Milliken et al., 2009b; Wray et al., 2009] and although mobilization and redeposition of older sediments cannot be ruled out, this may indicate that the formation of at least some phyllosilicates and sulfur-bearing minerals was near-contemporaneous. Lateral separation, where it does exist, can be explained by formation of different mineral assemblages in different environments, by preferential aqueous transport of the soluble salts relative to the insoluble phyllosilicates and their possible precursors or by leaching of coexisting phyllosilicates as sulfite- and Fe²⁺-bearing assemblages oxidized and released acidity.

[16] On Earth, the early Archean ocean, being much larger and longer lived than any Noachian surface water reservoir and therefore host to proportionally larger SO₂ sinks, would have been in equilibrium with lower atmospheric concentrations of SO₂. Indeed, the geologic record contains evidence for carbonate minerals throughout the Archean [Sumner and Grotzinger, 2000] and our experimental results imply that $p\text{SO}_2:p\text{CO}_2$ was lower than $\sim 1.3 \times 10^{-8}$ when these carbonates formed. Whereas our results can explain the apparent absence of carbonates from the Martian geologic record, given constraints on $p\text{CO}_2$ from climate models or geochemical proxies, they can be used to place upper limits on $p\text{SO}_2$ for times in Earth's early history when carbonates exist in the geologic record.

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